133–134° (Found: C 70.97; H 4.99; S 15.93. Calc. for $C_{12}H_{10}OS$ (202.27) C 71.25; H 4.98; S 15.85).

3-Acetoxythiophene. 65 g of butyl borate in 170 ml absolute ether was added in a single portion to 3-thienyllithium which had been prepared from 190 ml 1.15 N butyllithium and 32.6 g (0.2 mole) of 3-bromothiophene⁶ in 50 ml absolute ether at -70° . The mixture was stirred at -60° for 4 h and the boronic acid⁷ isolated and oxidized as above. After the ethereal phases had been washed with ferrous sulphate they were extracted with 80 ml of cold sodium hydroxide solution. The alkaline solution was shaken vigorously for 5 min with crushed ice and 15 ml of acetic anhydride, and then extracted with ether. Distillation *in vacuo* under nitrogen yielded 8.5 g (30 %) of 3-acetoxythiophene b.p. $82-84^{\circ}/10$ mm Hg $n_D^{20} = 1.5200$ (Found: C 50.65; H 4.40; S 22.21. Calc. for $C_6H_6O_2S$ (142.18) C 50.68; H 4.26; S 22.56).

The NMR-spectra were recorded in deuteriochloroform-cyclohexane solution on a Varian Associate model A 60 high resolution spectrometer.

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A Tetragonal Form of Zirconium Oxide Sulfide, ZrOS

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In his study of the system Zr–S Schönberg¹ found a tetragonal phase with cell dimensions $a = 3.55$ Å; $c = 6.31$ Å and space group $P 4/nmm-D_{4h}^{19}$, to which he ascribed a composition of ZrS and a structure of the B 11 type. Several reinvestigations of the system Zr–S have been undertaken since, e.g. by Hahn and co-workers², by McTaggart and Wadsley³ and by the present author. All these investigators agree that ZrS has a cubic superstructure of the NaCl type; no indications were found for the existence of a tetragonal monosulfide, nor indeed for any tetragonal phase in the system Zr–S. (Tetragonal "Zr₄S₃"²) has shown to be a ternary phase of composition ZrSiS⁴.)

In view of these discrepancies a re-examination of Schönberg's X-ray diagrams of the system Zr–S was undertaken. It was confirmed that in several of his preparations a tetragonal phase with the dimensions and symmetry derived by Schönberg was present. However, all preparations which contain this phase had been partly oxidized: the tetragonal phase was always accompanied by considerable proportions of cubic ZrOS and in some cases even by ZrO₂. It seemed probable, therefore, that the tetragonal phase also contains oxygen.

From the symmetry it is evident that the unit cell must contain an even number of all kinds of atoms; from spatial considerations a unit-cell content of $2 \times ZrOS$ seems the most probable. This hypothesis is strongly supported by the fact the ThOS, UOS and NpOS have the same symmetry and similar cell dimensions as the tetragonal zirconium oxysulfide; the unit cells of ThOS, UOS and NpOS contain two formula units and the structures are of the PbFCl ($E 0_1$)-type⁵. It seems most probable, therefore, that the alleged tetragonal ZrS is a new modification of ZrOS, and that its structure is also of the PbFCl type. Zr and S are situated in positions 2(c): $0\frac{1}{2}z$; $\frac{1}{2}0z$; oxygen in position 2(a): $0\ 0\ 0$; $\frac{1}{2}\frac{1}{2}0$.

Table 1. Observed and calculated intensities (CuK α radiation).

hkl	I_{obs}	I_{calc}	I_{calc}
		PbFCl-type	B11-type
001	m ⁺	48	33
002	m ⁺	46	128
101	v st	216	164
110	st ⁺ *	178	238
102	v st	216	190
111	—	1	12
003	w ⁻	7	15
112	st	132	136
103	m ⁺	60	9
200	st	122	95
201	w ⁻ *	7	6
113	m ⁺	48	30
004	—	0	0
202	m	33	75
211	st ⁻	76	59
104	st ⁻	73	124
212	st	127	112
203	w	13	22
114	v w	5	0
213}	st ⁻	{58	8
005}		{24	5
220	st ⁻	59	49
221	— *	3	3
105	—	1	2
204	—	0	0
222}	m (br)	{20	45
301}		{21	16
115	m ⁺ *	50	16
310}	st (br)	{64	77
214}		{88	154
302}	m *	{41	36
311}		{0	4

* Intensity estimation inaccurate because of coincidence with line of cubic ZrOS.

The observed intensities are not sufficient for deriving accurate values for the z parameters of Zr and S, but "ideal" values can be calculated by geometrical considerations. Each metal is equidistant from its eight metal neighbours if $z_M = \frac{1}{4}\sqrt{2} \times a/c$. Furthermore, it is equidistant from its five sulfur neighbours, if $z_S = \frac{1}{2} + \frac{a^2}{4c^2(1-2z_M)}$ or, introducing the ideal value of z_M :

$$z_S = \frac{1}{2} + \frac{a^2}{4c^2 - 2\sqrt{2}ac}. \text{ Substitution of the}$$

observed value for c/a leads to "ideal" parameter values of $z_{\text{Zr}} = 0.199$ and $z_S = 0.631$.

A comparison with ThOS, UOS, NpOS⁸ shows that the "observed" values of z_S closely correspond to the ideal ones, while z_M always is slightly less than the ideal value, the difference being 0.004 on the average. Therefore, the following parameter values were adopted: $z_{\text{Zr}} = 0.19_5$; $z_S = 0.63_0$. Using these values, the agreement between observed and calculated intensities (see Table 1) is as good as can be wished; indeed, the agreement is considerably better than that for the structure proposed by Schönberg which is also included in Table 1. (Table 1 of Schönberg's paper¹ should be disregarded, as several errors have crept into both I_{calc} and I_{obs} . The interatomic distances derived from the adopted parameters (Zr—5S = 2.74 Å; Zr—4O = 2.16 Å) are slightly larger than the distances in cubic ZrOS⁹, as is to be expected by the increase of the co-ordination number of the metal from seven to nine.

Although all attempts to prepare the phase in a state sufficiently pure for chemical analysis have failed so far, the conclusion that the alleged tetragonal ZrS actually is a new modification of ZrOS with a PbFCl-type structure seems well-supported.

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